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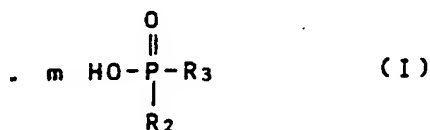
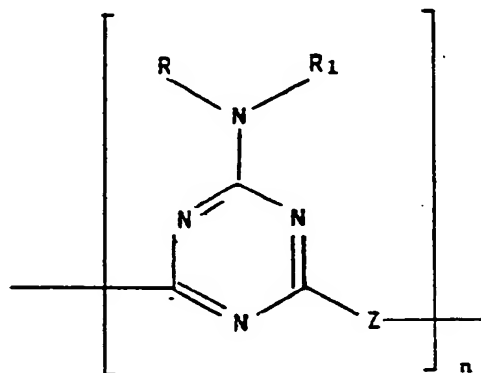
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(54) **Salts of triazinic compounds with phosphorus oxyacids, and use of said compounds in self-extinguishing polymeric compositions.**

(57) **Salts of triazinic compounds with phosphorus oxyacids, having the general formula (I):**



obtained by salifying oligomeric derivatives of 2,4, 6-triamino-1,3,5-triazine with a phosphorus-containing acid.  
The compounds with general formula (I) find use in particular as flame-retardant additives.

The present invention relates to salts of triazinic compounds with phosphorus oxyacids.

More particularly, the present invention relates to salts of triazinic compounds with phosphorus oxyacids, and to their use in the preparation of self-extinguishing polymeric compositions based on thermoplastic polymers, or on polymers with elastomeric properties, in particular olefinic polymers or copolymers.

In the art several solutions are known in order to reduce or eliminate the combustibility of polymers. Some of such solutions are based on the use of metal compounds, in particular of antimony, bismuth or arsenic, in combination with partially halogenated and thermally unstable organic compounds, such as chlorinated paraffinic waxes.

Other solutions are based on the use of substances able to produce intumescence. The formulations of intumescent type are generally constituted by the polymer and at least three main additives: an essentially phosphorus-containing additive, the purpose of which is of forming, during combustion, a semisolid, impermeable glassy layer essentially constituted by polyphosphoric acid, and of activating the process leading to intumescence formation; a second additive which contains nitrogen and performs the function of foaming agent; and a third additive, which contains carbon and acts as a carbon donor in order to form an insulating cellular carbonaceous layer (char) between the polymer and the flame.

Examples of such a type of intumescent formulations are those reported in the following patents: U.S. patent No. 3,810,862 (Phillips Petroleum Co.), based on melamine, pentaerythritol and ammonium polyphosphate; U.S. patent No. 4,727,102 (Vamp S.r.l.), based on melamine cyanurate, a hydroxyalkyl derivative of isocyanuric acid and ammonium polyphosphate; and published patent application WO 85/05626 (Plascoat U.K. Limited), based on several phosphorus and nitrogen compounds among which, in particular, a combination of melamine phosphate, pentaerythritol and ammonium polyphosphate may be mentioned.

In more recent formulations, together with the use of an organic or inorganic phosphorus compound, a nitrogen-containing compound was used, which generally is an aminoplastic resin obtained by condensing urea, melamine or dicyandiamide with formaldehyde.

Examples of double-additive formulations are those reported in U.S. patent No. 4,504,610 (Montedison S.p.A.), based on oligomeric derivatives of 1,3,5-triazine and ammonium polyphosphate; and EP patent 14,463 (Montedison S.p.A.), based on organic compounds selected from among benzylguanamine and reaction products of aldehydes with various nitrogen-containing cyclic compounds, in particular benzylguanamine/formaldehyde copolymers, and ammonium polyphosphate.

Self-extinguishing compositions can also be obtained by using single-component additives, containing both nitrogen and phosphorus in one single organic molecule, as disclosed in U.S. patent No. 4,201,705 (Borg-Wagner Corp.).

These intumescent flame-retardant systems endow the polymer which contains them, with the property of originating a carbonaceous residue after a fire or a flame application. This kind of retardant systems display a number of advantages: absence of phenomena of corrosion in the machines on which the polymers are processed, lower smoke generation as compared to systems containing metal compounds and halogenated hydrocarbons, and, above all, the possibility of endowing the polymers with satisfactory flame-retardant properties with a smaller amount of total additive, and, consequently, without an excessive decay of the mechanical properties of the same polymers.

The present Applicant has found now that extremely good flame-retardant properties can be supplied to the above said polymers by means of the use of a category of simple-structure phosphorus-nitrogen-containing compounds, based on oligomeric derivatives of 2,4,6-triamino-1,3,5-triazine salified with a phosphorus-containing acid.

The novel additives make it also possible, when suitably mixed with ammonium and/or amine phosphates and/or phosphonates, polymeric compositions to be obtained which are endowed with excellent self-extinguishing characteristics with a lower total content of additives as compared to the prior art, and, therefore, with a further contribution to the preservation of chemical and physical properties of the polymers in question.

The present Applicant has furthermore evidenced that the reaction of salification of oligomeric derivatives of 2,4,6-triamino-1,3,5-triazine with phosphorus oxy-acids not only makes it possible -- as it was obvious -- the amount of ammonium or amine phosphate and/or phosphonate to be reduced, but also self-extinguishment levels to be reached which could not be obtained by simply using the oligomeric triazinic derivatives with ammonium or amine phosphates and/or phosphonates.

The novel additives furthermore display good stability to heat, hence retaining a high activity as flame-retardants also after the high-temperature fabrication processes the polymeric compositions which contain them are submitted to.

The polymeric compositions containing the phosphorus-nitrogen additives according to the present invention furthermore show the advantage of giving rise, in the case of a fire, to a very moderate and non-obscuring smoke emission.

Therefore, the object of the instant invention are the salts with general formula (I):

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wherein:

R is H or

$[-C_pH_{2p}-]O-R_4$

25

in which

p is an integer comprised within the range of from 2 to 8, and preferably of from 2 to 4; and

R<sub>4</sub> is H; (C<sub>1</sub>-C<sub>8</sub>)-alkyl; preferably H or (C<sub>1</sub>-C<sub>4</sub>)-alkyl; (C<sub>2</sub>-C<sub>8</sub>)-alkenyl;  $[-C_qH_{2q}-]O-R_5$  in which

q is an integer comprised within the range of from 1 to 4; and

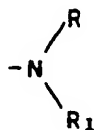
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R<sub>5</sub> is H or (C<sub>1</sub>-C<sub>4</sub>)-alkyl; (C<sub>6</sub>-C<sub>12</sub>)-cycloalkyl or alkylcycloalkyl;

R<sub>1</sub> is (C<sub>1</sub>-C<sub>4</sub>)-alkyl or R;

or the moiety:

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40 is replaced by a heterocyclic radical bonded to the triazinic ring through the nitrogen atom;

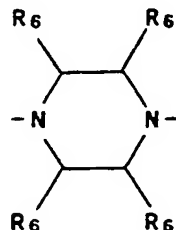
n is an integer comprised within the range of from 2 to 50;

m is a numeral smaller than, or equal to, n; in particular, the ratio of m/n is comprised within the range of from 0.5 to 1;

Z is a divalent or polyvalent radical falling within the scope of one of following formulae:

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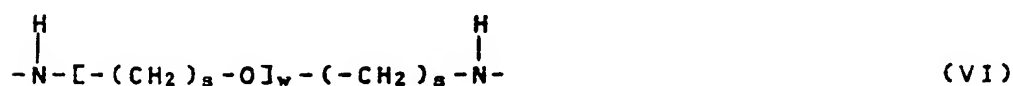
(II)

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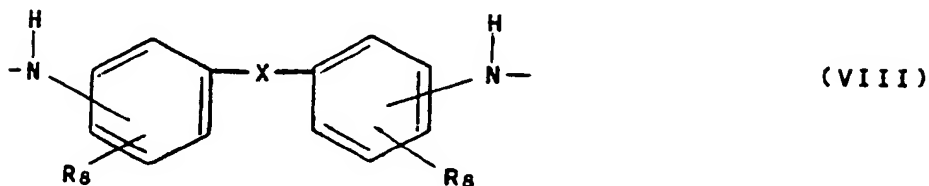
wherein the -R<sub>6</sub> radicals, which may be the same, or different from each other, are hydrogen or (C<sub>1</sub>-C<sub>4</sub>)-alkyl;



wherein  $t$  is an integer comprised within the range of from 2 to 14;  $R_7$  is hydrogen,  $(C_1-C_4)$ -alkyl,  $(C_2-C_6)$ -alkenyl,  $(C_1-C_4)$ -hydroxyalkyl;

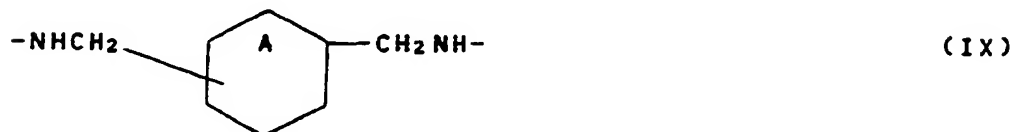


wherein  $s$  is an integer comprised within the range of from 2 to 5 and  $w$  is an integer comprised within the range of from 1 to 3;

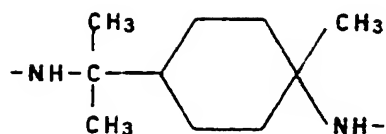


wherein:

$X$  is a direct  $\text{--C--C--}$ ;  $O$ ;  $S$ ;  $S\text{--}S$ ;  $SO$ ;  $SO_2$ ;  $NH$ ;  $NHSO_2$ ;  $NHCO$ ;  $N=N$ ;  $CH_2$  bond;  
 $R_8$  is hydrogen; hydroxy;  $(C_1-C_4)$ -alkyl;  $(C_1-C_4)$ -alkoxy;



wherein "A" can be a saturated or unsaturated cycle;

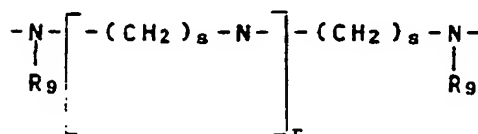


(X)



(XI)

wherein s has the above defined meaning;



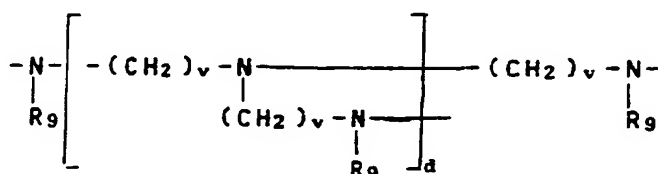
(XII)

wherein:

R<sub>9</sub> is hydrogen or (C<sub>1</sub>-C<sub>4</sub>)-alkyl;

r is an integer comprised within the range of from 1 to 5;

the indexes s, which are the same, or may be different from each other, have the above defined meaning;



(XIII)

wherein:

R<sub>9</sub> has the above defined meaning;

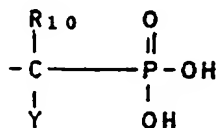
v is an integer comprised within the range of from 2 to 4;

d is either 1 or 2;

R<sub>2</sub> is H; OH; -O-(C<sub>1</sub>-C<sub>8</sub>)-alkyl; -O-(C<sub>6</sub>-C<sub>12</sub>)-aryl, possibly substituted with a (C<sub>1</sub>-C<sub>8</sub>)-alkyl; (C<sub>7</sub>-C<sub>16</sub>)-aralkyl; (C<sub>1</sub>-C<sub>4</sub>)-alkyl possibly substituted with a carboxy group; (C<sub>6</sub>-C<sub>12</sub>)-aryl;

R<sub>3</sub> is H; OH; -O-(C<sub>1</sub>-C<sub>8</sub>)-alkyl; -O-(C<sub>6</sub>-C<sub>12</sub>)-aryl, (C<sub>1</sub>-C<sub>4</sub>)-alkyl; (C<sub>6</sub>-C<sub>12</sub>)-aryl;

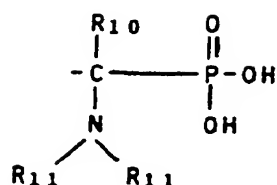
R<sub>3</sub> furthermore is:



wherein:

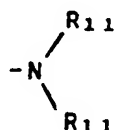
R<sub>10</sub> is hydrogen or (C<sub>1</sub>-C<sub>12</sub>)-alkyl;

Y is OH or R<sub>10</sub>;

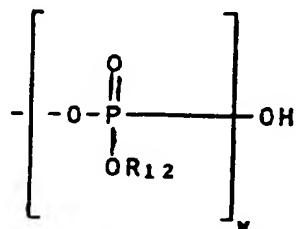


wherein:

$R_{10}$  has the same meaning as defined hereinabove and  $R_{11}$  radicals, which are the same, or may be different from each other, are hydrogen or (C<sub>1</sub>-C<sub>4</sub>)-alkyl; or the moiety:



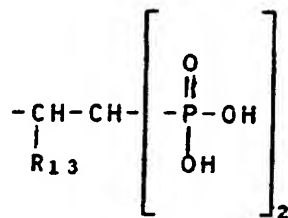
is replaced by a heterocyclic radical bonded to the carbon atom through the nitrogen atom and possibly containing another heteroatom preferably selected from O, S, N;



wherein:

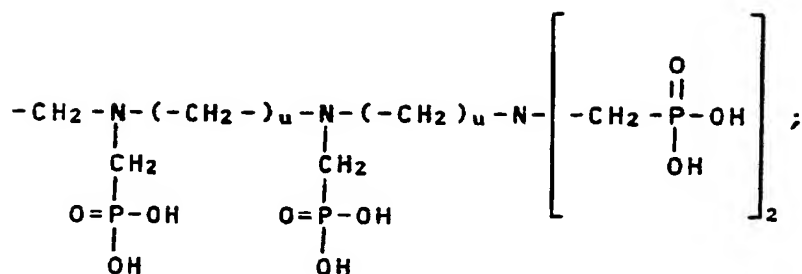
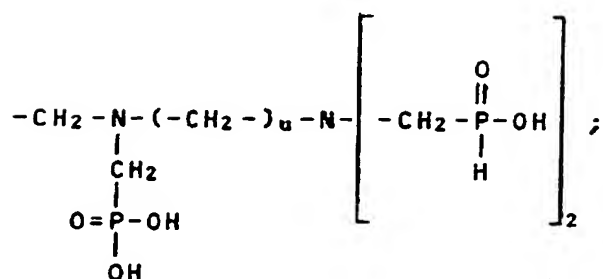
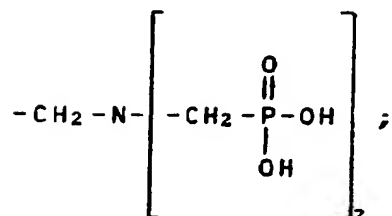
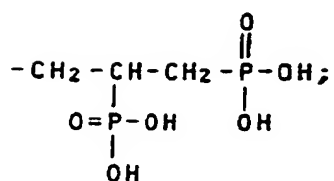
$R_{12}$  is hydrogen or (C<sub>1</sub>-C<sub>8</sub>)-alkyl; and

$w$  has the same meaning as defined hereinabove;



wherein:

$R_{13}$  is hydrogen or hydroxy;

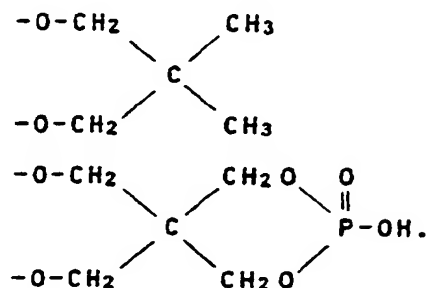


wherein:

u has the same meaning as defined above;

or

R<sub>2</sub> and R<sub>3</sub>, taken together, may constitute a cyclic structure having the formula:



Examples of R radical, in general formula (I), are:

2-hydroxyethyl; 2-hydroxypropyl; 3-hydroxypropyl; 3-hydroxybutyl; 4-hydroxybutyl; 3-hydroxypentyl; 5-hydroxypentyl; 6-hydroxyhexyl; 3-hydroxy-2,5-dimethyl-hexyl; 7-hydroxyheptyl; 7-hydroxyoctyl; 2-methox-

yethyl; 2-methoxypropyl; 3-methoxypropyl; 4-methoxybutyl; 6-methoxyhexyl; 7-methoxyheptyl; 7-methoxyoctyl; 2-ethoxyethyl; 3-ethoxypropyl; 4-ethoxybutyl; 3-propoxypropyl; 3-butoxypropyl; 4-butoxybutyl; 4-isobutoxybutyl; 5-propoxypentyl; 2-cyclohexyloxyethyl; 2-ethenyloxyethyl; 2-(2-hydroxyethoxy)ethyl; 2-(2-methoxyethoxy)ethyl; and so forth.

- 5 Examples of  $R_1$  radical are, besides those as defined for R: methyl; ethyl; propyl; isopropyl; butyl; isobutyl; tert.-butyl.

Examples of heterocyclic radicals which may replace the moiety:



- 15 are:

aziridine; pyrrolidine; piperidine; piperazine.

Examples of -Z- radicals are those deriving, by means of the removal of a hydrogen atom from each reacted amino group, from the following compounds:

- 20 piperazine; 2-methyl-piperazine; 2,5-dimethyl-piperazine; 2,3,5,6-tetramethyl-piperazine; 2-ethyl-piperazine; 2,5-diethylpiperazine; 1,2-diaminoethane; 1,3-diaminopropane; 1,4-diaminobutane; 1,5-diaminopentane; 1,6-diaminohexane; 1,8-diaminooctane; 1,10-diaminodecane; 1,12-diaminododecane; N,N'-dimethyl-1,2-diaminoethane; N-methyl-1,3-diaminopropane; N-ethyl-1,2-diaminoethane; N-isopropyl-1,2-diaminoethane; N-(2-hydroxyethyl)-1,2-diaminoethane; N,N'-bis-(2-hydroxyethyl)-1,2-diaminoethane; N-(2-hydroxyethyl)-1,3-diaminopropane; n-hexenyl-1,6-diaminohexane; N,N'-diethyl-1,4-diamino-2-butene; 2,5-diamino-3-hexene; 2-aminoethyl-ether; (2-aminoethoxy)-methyl-ether; 1,2-bis-(2-aminoethoxy)-ethane; 1,3-diaminobenzene; 1,4-di-aminobenzene; 2,4-diaminotoluene; 2,4-diaminoanisole; 2,4-diaminophenol; 4-aminophenylether; 4,4'-methylene-dianiline; 4,4'-diaminobenzanilide; 3-aminophenylsulfone; 4-aminophenylsulfone; 4-aminophenylsulfoxide; 4-aminophenyldisulfide; 1,3-bis(aminomethyl)benzene; 1,4-bis(aminomethyl)benzene; 1,3-bis(aminomethyl)cyclohexane; 1,8-diamino-p-menthane; 1,4-bis(2-aminoethyl)-piperazine; 1,4-bis(3-aminopropyl)piperazine; 1,4-bis(4-aminobutyl)piperazine; 1,4-bis-(5-aminopentyl)amine; bis[2-(N-methylamino)-ethyl]-amine; bis(3-aminopropyl)amine; bis(4-aminobutyl)amine; bis(5-aminopentyl)amine; bis[2-(N-methylamino)-ethyl]-amine; 2-N-butyl-bis-(2-aminoethyl)-amine; bis[3-(N-methylamino)-propyl]-amine; N-(3-aminopropyl)-1,4-di-aminobutane; N-(3-aminopropyl)-1,5-diaminopentane; N-(4-aminobutyl)-1,5-diaminopentane; tris(2-aminoethyl)-amine; tris(3-aminopropyl)-amine; tris(4-aminobutyl)-amine; tris[2-(N-ethylamino)-ethyl]-amine; N,N'-bis(2-aminoethyl)-1,2-diaminoethane; N,N'-bis(3-aminopropyl)-1,3-diaminopropane; N,N'-bis(2-aminoethyl)-1,3-diaminopropane; N,N'-bis(3-aminopropyl)-1,2-diaminoethane; N,N'-bis(3-aminopropyl)-1,4-diaminobutane; bis-[2-(2-aminoethyl)-aminoethyl]-amine; N,N'-bis[2-(2-aminoethyl)-aminoethyl]-1,2-diaminoethane; N,N'-bis[3-(2-aminoethyl)-aminopropyl]-1,2-diaminoethane; N,N,N',N'-tetrakis-(2-aminoethyl)-1,2-diaminoethane; and so forth.

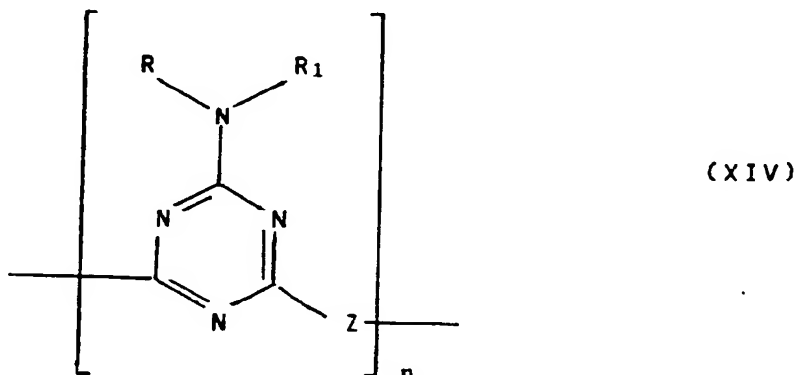
Examples of phosphorus containing acids are:

- hypophosphorous acid; phosphorous acid; phosphoric acid; pyrophosphoric acid; tripolyphosphoric acid; ethane-1,1,2-triphosphonic acid; 2-hydroxyethane-1,1,2-triphosphonic acid; propane-1,2,3-triphosphonic acid; isopropylphosphoric acid; n-butylphosphoric acid; di-n-butylphosphoric acid; di-isopropylphosphoric acid; di-n-pentylphosphoric acid; isooctylphosphoric acid; hexylphosphoric acid; 2-ethylhexylphosphoric acid; methylphosphonic acid; ethylphosphonic acid; n-propylphosphonic acid; n-butylphosphonic acid; aminomethylphosphonic acid; phenylphosphoric acid; phenylphosphonic acid; phenylphosphinic acid; di-n-butylpyrophosphoric acid; di-(2-ethylhexyl)pyrophosphoric acid; octylphenylphosphoric acid; 2-methylbenzylphosphonic acid; 1-aminoethane-1,1-diphosphonic acid; 1-hydroxyethane-1,1-diphosphonic acid; 1-hydroxydodecane-1,1-diphosphonic acid; 1-(N-methylamino)-ethane-1,1-diphosphonic acid; N,N-dimethylaminoethane-1,1-diphosphonic acid; N-butyl-aminomethane-1,1-diphosphonic acid; phosphonoacetic acid; 2-phosphonopropionic acid; 3-phosphonopropionic acid; 2-phosphonobutyric acid; 4-phosphonobutyric acid; 2-hydroxy-5,5-dimethyl-2-oxo-1,3,2-dioxophosphorinane; 3,9-dihydroxy-2,4,8,10-tetraoxo-3,9-diphosphaspiro[5,5]undecane-3,9-dioxide; amino-tris(methylenephosphonic) acid; ethylenediaminetetra(methylenephosphonic) acid; hexamethylenediaminetetra(methylenephosphonic) acid; diethylenetriaminopenta(methylenephosphonic) acid; and so forth.

Specific compounds falling within the scope of formula (I) are reported in the Examples which follow the instant disclosure.



The products of general formula (I) can be synthesized by reacting -- in the presence of a suitable solvent (such as, e.g., water, methyl alcohol, ethyl alcohol, acetonitrile,) at temperatures comprised within the range of from 0° C to the boiling point of the solvent used -- an oligomeric derivative of 2,4,6-triamino-1,3,5-triazine, having the general formula (XIV):



wherein R, R<sub>1</sub>, Z and n have the same meaning as defined hereinabove, with a phosphorus-containing acid having the general formula (XV):

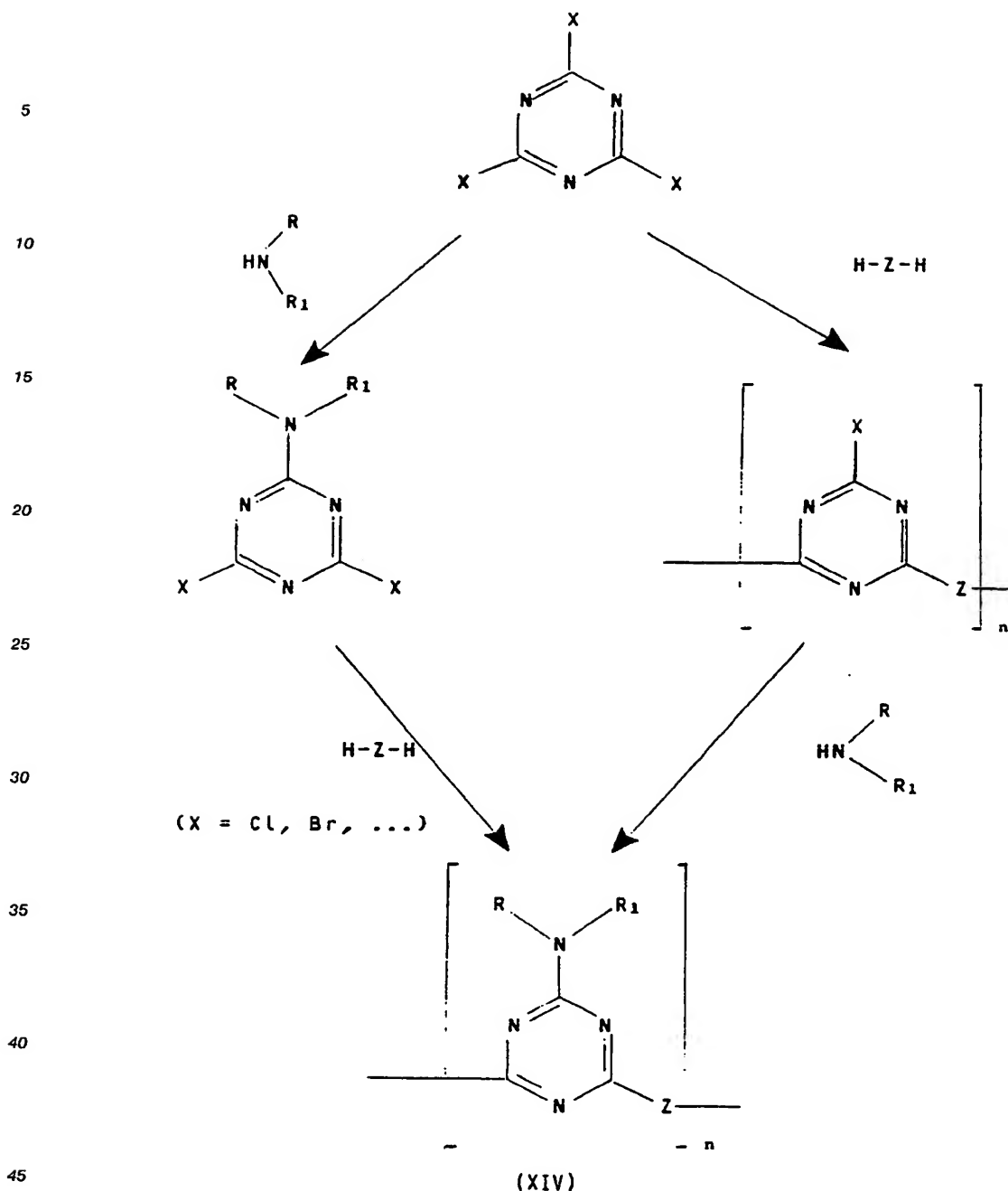


wherein R<sub>2</sub> and R<sub>3</sub> have the same meaning as defined hereinabove, or, if the phosphorus-containing acid may act as a solvent, in the absence of solvents and with an excess of phosphorus-containing acid, at temperatures comprised within the range of from 0 to 150° C.

The resulting salt product can be easily separated from the reaction mass by filtration, or by distilling off the solvent.

In general, products of general formula (I) are obtained as crystalline powders of white colour, which are of good quality and can be used in self-extinguishing composition without any further purification steps.

Some of the intermediates of general formula (XIV) are known; however, they can be easily synthesized according to the general method schematically shown hereinunder:



or according to as disclosed in Italian patent application No. 21 456 A/90 filed by the present Applicant on Sep. 13th, 1990.

Also the phosphorus-containing acids having the general formula (XV) are known, and many of them are also available in commercial amounts.

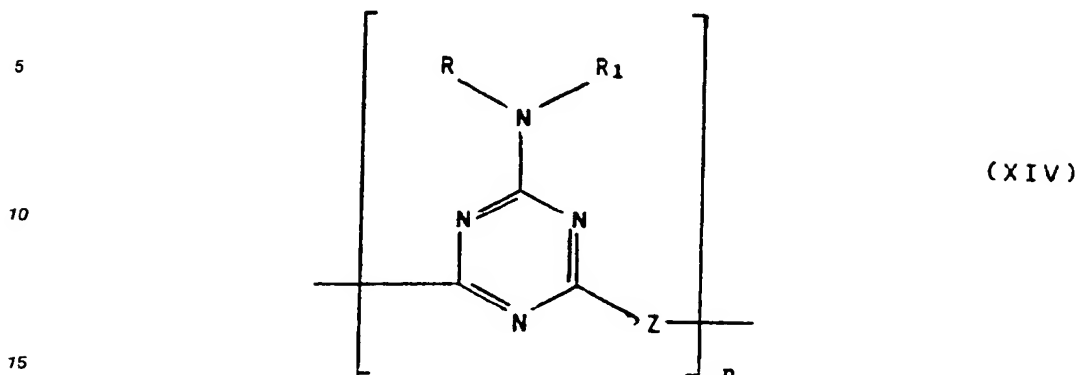
Another object of the present invention are the self-extinguishing polymeric compositions comprising:

(a) from 90 to 40 parts by weight of a thermoplastic polymer, or of a polymer endowed with elastomeric properties;

(b) from 7 to 28, preferably from 8 to 25, parts by weight of one or more ammonium or amine phosphate(s) or phosphonate(s);

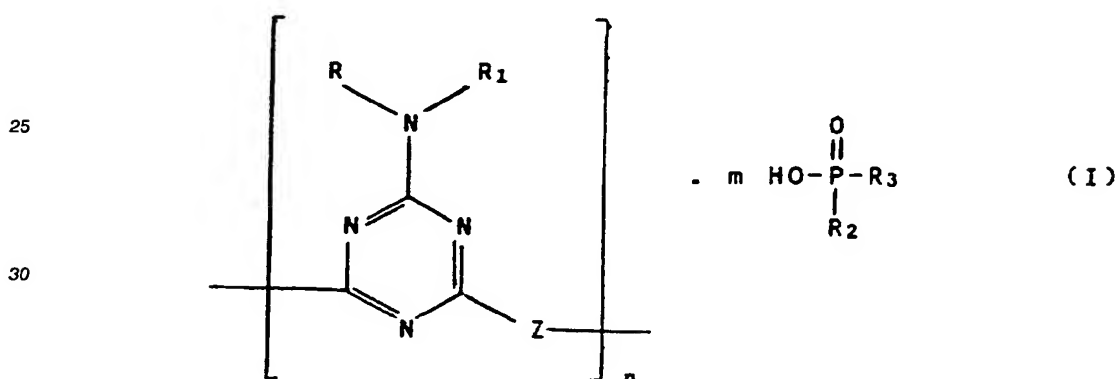
(c) from 3 to 32, preferably from 4 to 25, parts by weight of one or more oligomeric derivative(s) of 2,4,6-triamino-1,3,5-triazine salified with a phosphorus oxyacid, said oligomeric derivatives of 2,4,6-triamino-

1,3,5-triazine having the general formula (XIV):



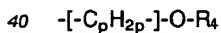
wherein R, R<sub>1</sub>, Z and n have the same meaning as defined hereinabove.

The (c) component is preferably selected from the salts having the general formula (I):

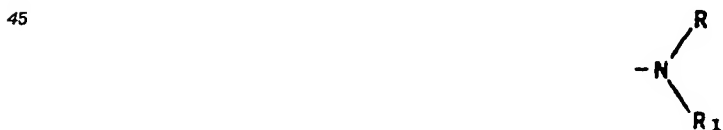


wherein the radicals from R to R<sub>3</sub>, Z, n and m have the same meaning as defined hereinabove.

Particularly preferred are the salts of those compounds of general formula (XIV), wherein the R radical is replaced by a

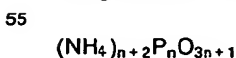


moiety, in which p is an integer comprised within the range of from 2 to 4 and R<sub>4</sub> is hydrogen or (C<sub>1</sub>-C<sub>4</sub>)-alkyl; or R<sub>1</sub> radical is hydrogen, or the moiety:



is replaced by an -NH<sub>2</sub> radical or a heterocyclic radical selected from among aziridine, pyrrolidine, piperidine, piperazine.

Among the phosphates, those ammonium polyphosphates are preferred which fall within the scope of the general formula



in which n represents an integer equal to, or larger than, 2; preferably, the molecular weight of

polyphosphates should be high enough, in order to secure a low solubility in water. For indicative purposes, n is preferably comprised within the range of from 2 to 500.

The composition of the polyphosphates having the formula indicated hereinabove, in which n is a large enough numeral and is preferably comprised within the range of from 50 to 500, practically is the composition which corresponds to the formula of metaphosphates



An example for such polyphosphates is the product known under the trade name "Exolit 422" (manufactured and marketed by Hoechst) and having the composition  $(\text{NH}_4\text{PO}_3)_n$ , in which n is larger than 50; another example is the product known under the trade name "Phos-Chek P/30" (Monsanto Chemical) and having an analogous composition.

Another polyphosphate which may be advantageously used, above all thanks to its low solubility in water, is the product known under the trade name "Exolit 462" (manufactured and marketed by Hoechst) and corresponding to Exolit 422 microencapsulated in melamine-formaldehyde resin.

Other phosphates which can be used are those deriving from amines, such as, e.g., dimethylammonium or diethylenetriammonium phosphate, ethylenediamine phosphate, melamine ortho- or pyrophosphate.

Among phosphonates, extremely good results were obtained by using those (mono- or poly-substituted) ammonium phosphonates which are derived from mono- and poly-phosphonic acids, examples of which are: ethane-1,1,2-triphosphonic acid; 2-hydroxyethane-1,1,2-triphosphonic acid; propane-1,2,3-triphosphonic acid; methyl-phosphonic acid; ethyl-phosphonic acid; n-propylphosphonic acid; n-butylphosphonic acid; phenylphosphonic acid; 1-amino-ethane-1,1-diphosphonic acid; 1-hydroxyethane-1,1-diphosphonic acid; 1-hydroxydodecane-1,1-diphosphonic acid; phosphonoacetic acid; 2-phosphonopropionic acid; 3-phosphonopropionic acid; 2-phosphonobutyric acid; 4-phosphonobutyric acid; amino-tris(methylenephosphonic) acid; ethylenediaminetetra(methylenephosphonic) acid; hexamethylenediaminetetra(methylenephosphonic) acid; diethylenetriaminopenta(methylenephosphonic) acid; and so forth.

Among the polymers which can be used in the compositions according to the present invention, those polymers and copolymers of olefines are preferred which have the general formula

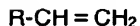


in which R is a hydrogen atom, or a  $\text{C}_1$ - $\text{C}_8$  alkyl or aryl radical; in particular:

1. isotactic or prevailing isotactic polypropylene;
2. HDPE, LLDPE, LDPE polyethylene;
3. crystalline propylene copolymers containing minor proportions of ethylene and/or other alpha-olefins, such as, e.g., 1-butene, 1-hexene, 1-octene, 4-methyl-1-pentene;
4. heterophasic compositions comprising
  - (A) a fraction consisting of a propylene copolymer, or of one of the copolymers according to (3); and
  - (B) a copolymeric fraction formed by elastomeric copolymers of ethylene with an alpha-olefin, possibly containing minor proportions of a diene, with said alpha-olefin being preferably selected from propylene and 1-butene;
5. elastomeric copolymers of ethylene with alpha-olefins possibly containing minor proportions of a diene.

Examples of dienes which are more commonly used in said elastomeric copolymers are butadiene, ethylidene-norbornene, hexadiene-1,4.

Among the polymers of olefins with formula



in which R is an aryl radical, "Crystal" and impact resistant polystyrene are preferred.

Other examples of polymers which can be commonly used are acrylonitrile/butadiene/styrene (ABS) and styrene/acrylonitrile (SAN) copolymers; (polyester and polyether) polyurethane; poly-(ethylene terephthalate); poly-(butylene terephthalate) and polyamides.

The self-extinguishing compositions according to the present invention can be prepared by means of methods known from the prior art: for example, ammonium or amine phosphate or phosphonate is first intimately mixed with one or more salts of the compounds of general formula (XIV) in finely subdivided form (with their particles being preferably smaller than 70 micrometres) and the resulting mixture is added to the polymer in a turbomixer, in order to produce a homogeneous blend which is subsequently extruded and

pelletized. The granular product obtained in that way can be transformed into various articles of manufacture by means of any of the well-known, available moulding techniques.

The flame-retardant additives according to the present invention are also suitable for use in the field of flame-retardant paints.

5 Oligomeric compounds with salt character falling within the scope of general formula (I) not cited in the examples, but equally advantageously useable in the self-extinguishing polymeric compositions according to the present invention, are those reported in following Table 1.

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Table 1

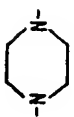

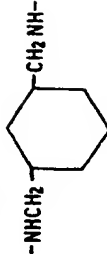

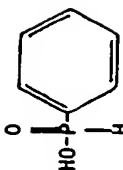
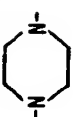
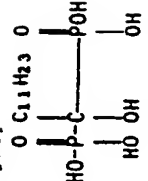
Compounds	R-----N-----R <sub>1</sub>	- Z -	n	m/n	$  \begin{array}{c}  \text{O} \\    \\  \text{HO}-\text{P}-\text{R}_3 \\    \\  \text{R}_2  \end{array}  $
1	CH <sub>2</sub> CH <sub>2</sub> OH		14	0.7	H <sub>3</sub> PO <sub>3</sub>
2	CH <sub>2</sub> CH <sub>2</sub> OH		15	1	H <sub>3</sub> PO <sub>4</sub>
3	CH <sub>2</sub> CH <sub>2</sub> OC <sub>2</sub> H <sub>5</sub>		13	1	H <sub>3</sub> PO <sub>4</sub>
4	(CH <sub>2</sub> ) <sub>5</sub> OH		18	0.6	
5	CH <sub>2</sub> CH <sub>2</sub> OCH <sub>3</sub>	N(CH <sub>2</sub> CH <sub>2</sub> - NH-) <sub>3</sub>	12	1	H <sub>3</sub> PO <sub>4</sub>
6	CH <sub>2</sub> CH <sub>2</sub> OH   CH <sub>3</sub>		21	0.4	

Table 1 (continued)



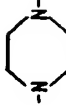
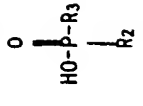
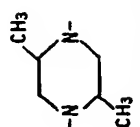
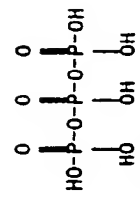
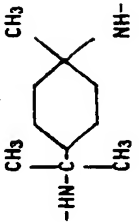
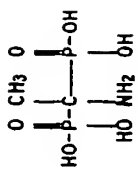
Compounds	R-----N-----R <sub>1</sub>	- Z -	n	m/n	$\begin{array}{c} \text{O} \\   \\ \text{HO}-\text{P}-\text{R}_3 \\   \\ \text{R}_2 \end{array}$
7	CH <sub>2</sub> CH <sub>2</sub> OCH=CH <sub>2</sub>		20	1	H <sub>3</sub> PO <sub>4</sub>
8	H		15	0.7	$\begin{array}{c} \text{O} \quad \text{CH}_3 \\   \quad / \\ \text{HO}-\text{P} \quad \text{C} \\   \quad \backslash \\ \text{OCH}_2 \quad \text{CH}_3 \end{array}$
9	(CH <sub>2</sub> ) <sub>2</sub> O(CH <sub>2</sub> ) <sub>2</sub> OCH <sub>3</sub>		14	1	H <sub>3</sub> PO <sub>4</sub>
10	H	-HNCH <sub>2</sub> CH <sub>2</sub> NH-	17	0.5	$\begin{array}{c} \text{O} \\   \\ \text{HO}-\text{P}-\text{O}-\text{nC}_4\text{H}_9 \\   \\ \text{HO} \end{array}$
					$\begin{array}{c} \text{O} \\   \\ \text{HO}-\text{P}-\text{O}-\text{nC}_4\text{H}_9 \\   \\ \text{O} \end{array}$
					$\begin{array}{c} \text{O} \\   \\ \text{HO}-\text{P}-\text{O}-\text{nC}_4\text{H}_9 \\   \\ \text{O} \end{array}$

Table 1 (continued)

Compounds	R-----N-----R <sub>1</sub>	- Z -	n	m/n	$\begin{array}{c} \text{O} \\   \\ \text{HO}-\text{P}-\text{R}_3 \\   \\ \text{R}_2 \end{array}$
11	CH <sub>2</sub> CH <sub>2</sub> OCH <sub>3</sub>	$\begin{array}{c} \text{CH}_3 \\   \\ \text{N}-\text{CH}_2\text{CH}_2-\text{N}- \\   \\ \text{CH}_3 \end{array}$	18	1	H <sub>3</sub> PO <sub>3</sub>
12	$\begin{array}{c} \text{CH}_2\text{CH}_2\text{O} \\   \\ \text{C}_6\text{H}_{11} \end{array}$	$\begin{array}{c} \text{N} \\   \\ \text{C}_6\text{H}_{11} \end{array}$	15	0.8	H <sub>3</sub> PO <sub>4</sub>
13	CH <sub>2</sub> CH <sub>2</sub> OCH <sub>3</sub>	-HN(CH <sub>2</sub> ) <sub>2</sub> N(CH <sub>2</sub> ) <sub>2</sub> N(CH <sub>2</sub> ) <sub>2</sub> NH-	11	0.5	H <sub>3</sub> PO <sub>4</sub>
14	H	-N-CH <sub>2</sub> CH <sub>2</sub> -N-	16	1	H <sub>3</sub> PO <sub>4</sub>
15	CH <sub>2</sub> CH <sub>2</sub> OH	$\begin{array}{c} \text{CH}_2\text{CH}_2\text{OH} \\   \\ \text{CH}_2\text{CH}_2\text{OH} \end{array}$	15	1	H <sub>3</sub> PO <sub>4</sub>
16	(CH <sub>2</sub> ) <sub>3</sub> OCH <sub>3</sub>	-HN(CH <sub>2</sub> ) <sub>2</sub> O(CH <sub>2</sub> ) <sub>2</sub> NH-	16	0.7	H <sub>3</sub> PO <sub>4</sub>
17	CH <sub>2</sub> CH <sub>2</sub> OCH <sub>3</sub>	$\begin{array}{c} \text{NH} \\   \\ \text{C}_6\text{H}_4 \\   \\ \text{CONH} \\   \\ \text{C}_6\text{H}_4 \\   \\ \text{NH} \end{array}$	17	1	H <sub>3</sub> PO <sub>3</sub>



Table 1 (continued)

Compounds	R-----N-----R <sub>1</sub>	- Z -	n	m/n	
18	H		14	0.3	
19	(CH <sub>2</sub> ) <sub>4</sub> OCH <sub>3</sub>	-N-CH <sub>2</sub> CH <sub>2</sub> -NH-   CH <sub>2</sub> CH <sub>2</sub> OH	18	1	H <sub>3</sub> PO <sub>4</sub>
20	(CH <sub>2</sub> ) <sub>2</sub> O(CH <sub>2</sub> ) <sub>2</sub> OH	-HNCH <sub>2</sub> CH <sub>2</sub> NH-	15	0.8	H <sub>3</sub> PO <sub>3</sub>
21	CH <sub>2</sub> CH <sub>2</sub> OH	-HN(CH <sub>2</sub> ) <sub>2</sub> -N-(CH <sub>2</sub> ) <sub>2</sub> NH-	20	1	H <sub>3</sub> PO <sub>4</sub>
22	CH <sub>2</sub> CH <sub>2</sub> OCH <sub>3</sub>	-HN(CH <sub>2</sub> ) <sub>3</sub> -N-(CH <sub>2</sub> ) <sub>3</sub> NH-	19	1	H <sub>3</sub> PO <sub>4</sub>
23	(CH <sub>2</sub> ) <sub>3</sub> OH	-HN(CH <sub>2</sub> ) <sub>3</sub> -N-(CH <sub>2</sub> ) <sub>3</sub> NH-	16	0.6	H <sub>3</sub> PO <sub>4</sub>
24	CH <sub>2</sub> CH <sub>2</sub> OH		14	0.4	

The following examples illustrate the features of the present invention, without limiting them.

The salifying reaction between the intermediates with general formula (XIV) and the phosphorus-containing acids with general formula (XV) are confirmed by I.R. spectroscopic analysis carried out on the I.R. spectrophotometer Model Perkin Elmer 580 B with raster.

In fact, it was observed that an extremely good reference signal is constituted by the band relevant to the off-plane deformation of the triazinic ring: said band is at approximately  $830\text{--}800\text{ cm}^{-1}$  in the case of the not perturbed ring, and is at  $795\text{--}760\text{ cm}^{-1}$  in the case of the ring with salified amino groups.

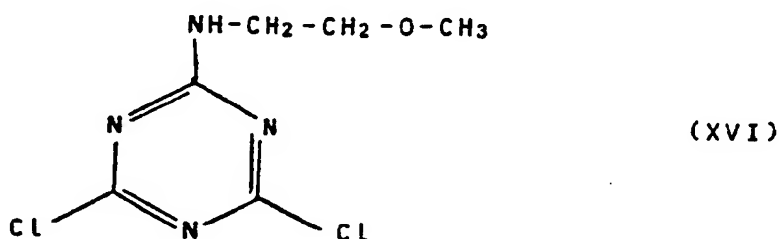
#### 5 Example 1

184.5 g of cyanuric chloride and 700 cm<sup>3</sup> of water are added to a reactor of 2 litres of capacity, equipped with stirrer, thermometer, addition funnel, reflux condenser and cooling bath.

With cooling from the outside, 75 g of 2-methoxyethylamine and 40 g of sodium hydroxide dissolved in 150 cm<sup>3</sup> of water are simultaneously added during a 3-hours time, With pH being kept at a value comprised within the range of from 5 to 7 and temperature being comprised within the range of from 0 to 3 °C.

The reaction mixture is kept at the temperature of 0-3 °C for a further 2 hours, then the resulting product is filtered off and is washed on the filter with water.

By drying the filter cake inside an oven at 50 °C, under vacuum, 214.5 g of intermediate (XVI):



is obtained as a white crystal powder with melting point (m.p.) = 73-75 °C, and with a chlorine content of 31.68% (theoretical value: 31.84%).

The structure of the intermediate was furthermore confirmed by N.M.R. analysis.

To the same reaction vessel of 2 litres of capacity, but equipped with heating bath, 800 cm<sup>3</sup> of xylene, 50 cm<sup>3</sup> of water and 100 g of intermediate (XVI) and then, with stirring, and during 20 minutes, 26.9 g of ethylenediamine, are added.

The temperature of the dispersion increases up to 60-65 °C; it is adjusted at 75 °C by means of the external heating bath, and is stirred at that temperature for about 1 hour.

Then, 17.5 g of sodium hydroxide dissolved in 40 cm<sup>3</sup> of water is added during a 2-hours time, and at the temperature of 75 °C.

The temperature is increased up to 95 °C and the reaction mixture is kept stirred at that temperature for about 2 hours.

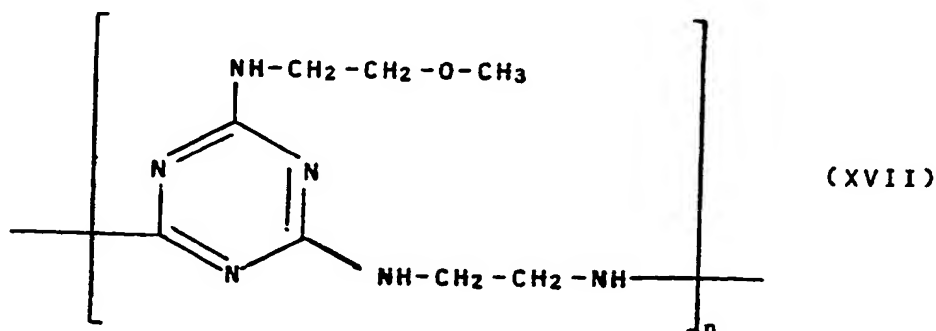
Then, 18.4 g of sodium hydroxide dissolved in 40 cm<sup>3</sup> of water is added during about 2 hours.

The temperature is gradually increased with water being removed by azeotropic distillation, until the boiling temperature of the solvent is reached.

The reaction mixture is kept refluxing for 10 hours, then the resulting mass is cooled down to room temperature, and the resulting product is filtered.

The filter cake is thoroughly pressed and is washed with plentiful water.

After oven drying at 100 °C, 84.9 g of intermediate (XVII):



is obtained as a crystalline powder of white colour, with m.p. = 182-186 °C and with n = 20.

500 cm<sup>3</sup> of acetonitrile, 63.0 g of intermediate (XVII) and, with stirring, 36.3 g of phosphoric acid at 85% by weight are added to a 1-litre reactor equipped with stirrer, thermometer, addition funnel, reflux condenser and heating bath.

5 The resulting reaction mixture is heated up to boiling, and is kept refluxing for 12 hours.

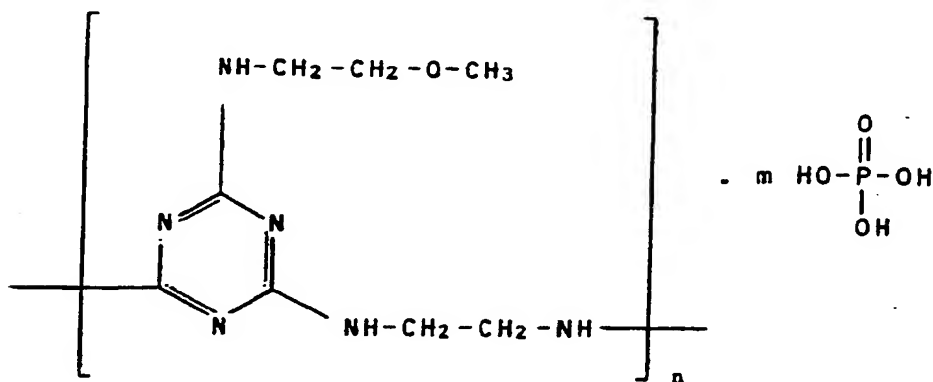
After cooling down to room temperature, the resulting product is filtered off and the filter cake is washed on the filter with acetonitrile.

After oven-drying the filter cake at 100 °C, 89.1 g of the product:

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25 is obtained as a crystalline powder of white colour with m.p. = 165-170 °C, with n = 20 and m/n = 1, and with a phosphorus content of 9.82% (theoretical value: 10.06%).

### Example 2

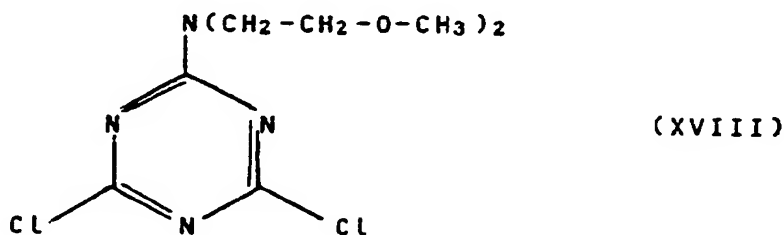
30 To the same reactor of Example 1, 800 cm<sup>3</sup> of water and 184.5 g of cyanuric chloride are added.

By following the same procedure as disclosed in Example 1, 133 g of bis(2-methoxyethylamine) is added.

By continuing to operate according to the modalities shown in said Example, 260.8 g of intermediate (XVIII):

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is obtained as a white crystal powder With m.p. = 62-65 °C, and with a chlorine content of 25.08% (theoretical value: 25.27%).

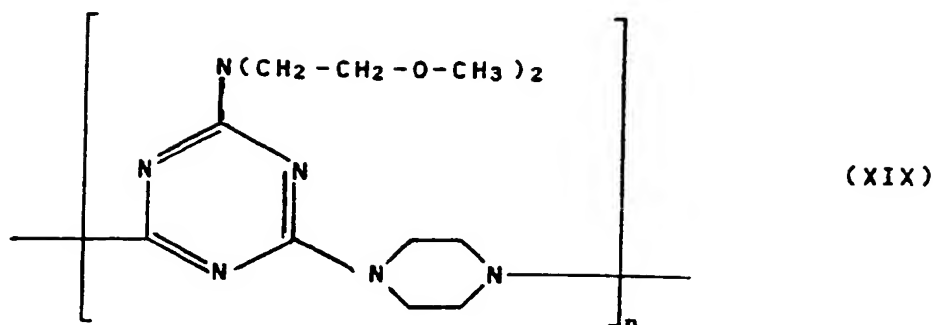
The structure of the intermediate (XVIII) was furthermore confirmed by N.M.R. analysis.

50 To the same reaction vessel of 2 litres of capacity as of Example 1, 800 cm<sup>3</sup> of xylene, 50 cm<sup>3</sup> of water and 135 g of intermediate (XVIII) and then, with stirring, and during 15 minutes, 41.3 g of piperazine are added.

The temperature of the suspension increases up to 40-45 °C.

Then, still following the same operating modalities as disclosed in Example 1 (in this case, 38 g of sodium hydroxide is used), 136.4 of intermediate (XIX):

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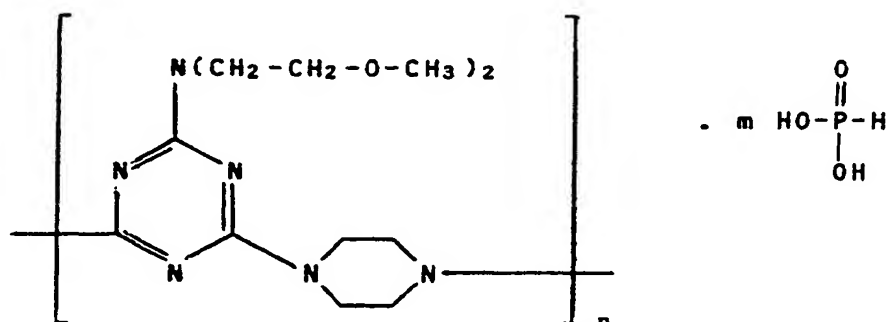
is obtained as a crystalline powder of white colour, with m.p.  $>300^{\circ}\text{C}$  and with  $n = 18$ .

600  $\text{cm}^3$  of acetonitrile, 88.2 g of intermediate (XIX) and, with stirring, 25.8 g of phosphorous acid are added to the same 1-litre reactor as of Example 1.

The resulting reaction mixture is heated up to its boiling temperature, and is kept refluxing for 12 hours.

After cooling down to room temperature, the resulting product is filtered off and the filter cake is washed on the filter with acetonitrile.

After oven-drying the filter cake at  $100^{\circ}\text{C}$ , 109.7 g of product:



is obtained as a crystalline powder of white colour with m.p.  $= 283-287^{\circ}\text{C}$ , with  $n = 18$  and  $m/n = 1$ , and with a phosphorus content of 8.01% (theoretical value: 8.24%).

### Example 3

400  $\text{cm}^3$  of acetone and 100 g of cyanuric chloride are added to the same 2-litre reactor as of Example 1.

The suspension is cooled down to  $0-5^{\circ}\text{C}$  and 23.4 g of piperazine is then added, during a 1-hour time.

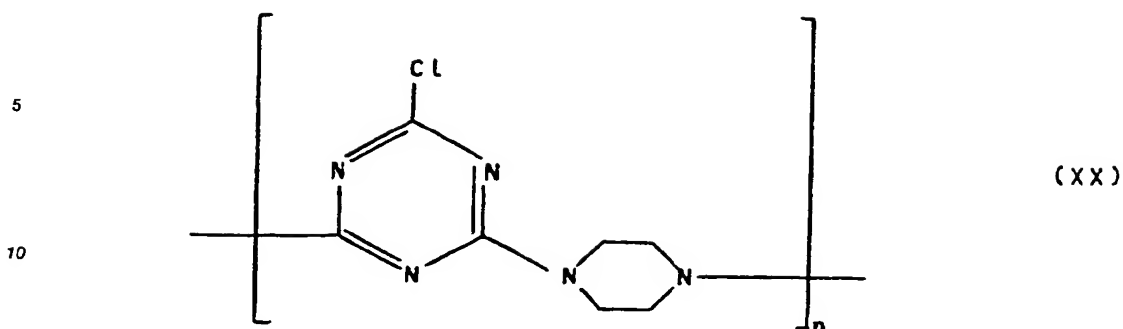
Still at  $0-5^{\circ}\text{C}$ , and during a 2-hour time, 23.3 g of piperazine and 10.8 g of sodium hydroxide dissolved in 50  $\text{cm}^3$  of water are fed simultaneously, in such a way as to keep pH at a value of round 3.

The temperature is increased up to  $20^{\circ}\text{C}$  during about 2 hours and 10.8 g of sodium hydroxide dissolved in 50  $\text{cm}^3$  of water are simultaneously added, so as to keep pH at a value of round 5.

The temperature is further gradually increased from 20 to  $60^{\circ}\text{C}$ , with a solution consisting of 21.8 g of sodium hydroxide in 100  $\text{cm}^3$  of water being simultaneously fed.

The reaction mass is kept stirred at  $60^{\circ}\text{C}$  for a further 2 hours, and then is cooled down to room temperature, and the resulting product is filtered off, and is washed on the filter, with water.

By drying the filter cake in an oven at  $100^{\circ}\text{C}$ , 104.9 g of intermediate (XX):



15 is obtained as a crystalline powder of white colour, with m.p.  $>300^{\circ}\text{C}$  and with  $n = 15$ , and with a chlorine content of 17.70% (theoretical value: 17.94%).

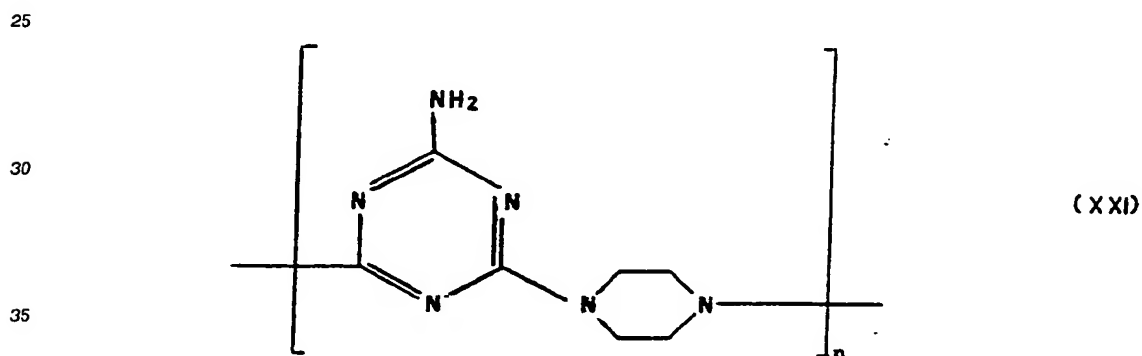
The structure of the intermediate was furthermore confirmed by I.R. spectroscopic analysis.

400  $\text{cm}^3$  of water, 125 g of a solution of ammonium hydroxide at 30% by weight and 100 of intermediate (XX) are added to a steel reactor of 1 litre of capacity.

20 The reaction mixture is then heated to  $150^{\circ}\text{C}$  and is kept at that temperature for 12 hours.

The reaction mixture is cooled down to room temperature, the resulting product is filtered off and the filter cake is washed on the filter, with water.

By oven-drying the filter cake in the oven at  $100^{\circ}\text{C}$ , 87.1 of intermediate (XXI):

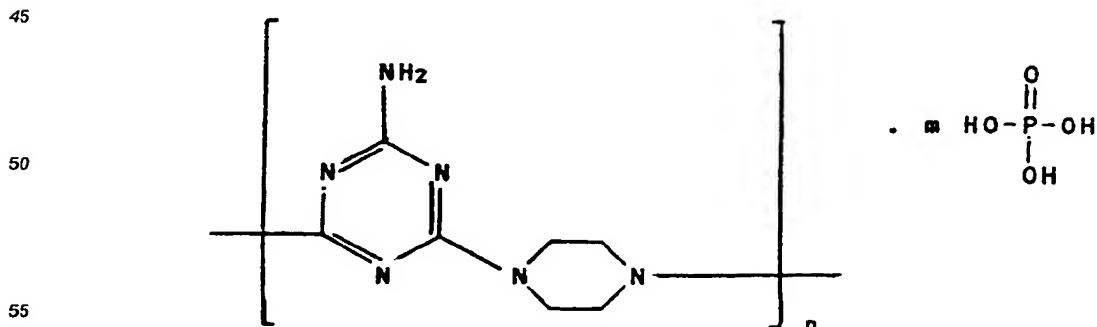


is obtained as a crystalline powder of white colour, with m.p.  $>300^{\circ}\text{C}$  and with  $n = 15$ .

40 600  $\text{cm}^3$  of acetonitrile, 53.4 g of intermediate (XXI) and, with stirring, 36.3 of phosphoric acid at 85% by weight are charged to a 1-litre reactor, equipped as in the preceding Examples.

The reaction mass is heated up to boiling temperature, and is kept refluxing for 14 hours.

Then, by proceeding analogously to as disclosed in Example 1, 82.1 g of product:



is obtained as a crystalline powder of white colour with m.p.  $>300^{\circ}\text{C}$ , with  $n = 15$  and  $m/n = 1$ , and with a phosphorus content of 11.06% (theoretical value: 11.23%).

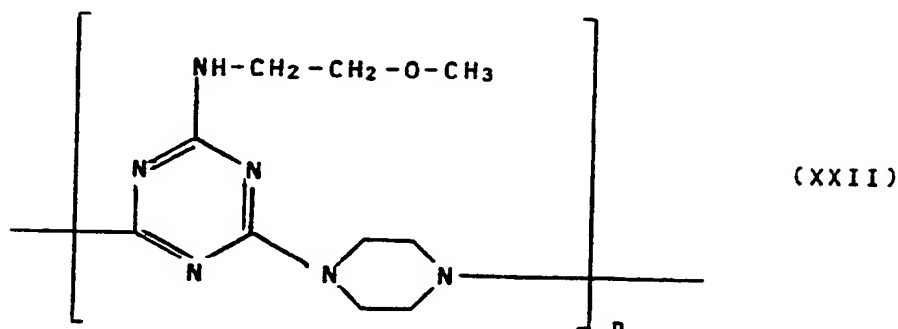
#### Example 4

To a 2-litre reactor equipped as in Example 1, 800  $\text{cm}^3$  of xylene, 100 g of intermediate (XVI), 38.6 g of piperazine and 35.9 g of sodium hydroxide are added.

The reaction mass is heated up to its boiling temperature, and is kept refluxing for 24 hours.

At the end, the reaction mixture is cooled down to room temperature, the resulting product is filtered off and the filter cake is washed on the filter with plentiful water.

By drying the filter cake 100.8 g of intermediate (XXII):

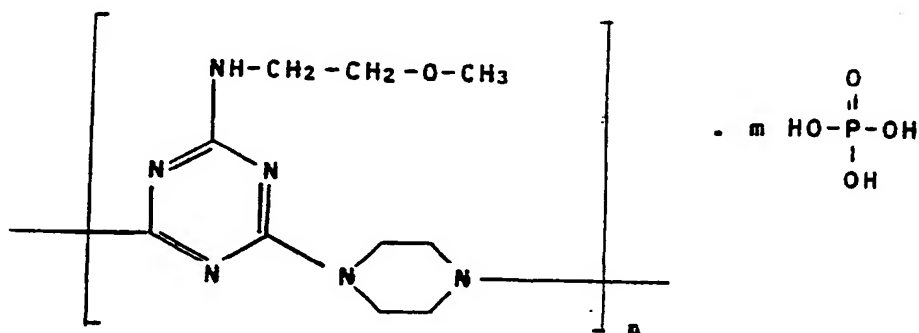


is obtained as a crystalline powder of white colour with m.p.  $>300^{\circ}\text{C}$ , and with  $n = 16$ .

500  $\text{cm}^3$  of acetonitrile, 59 g of intermediate (XXII) and, with stirring, 30.2 of phosphoric acid at 85% by weight are charged to a 1-litre reactor, equipped as in the preceding Example 1.

The reaction mass is heated up to boiling temperature, and is kept refluxing for 14 hours.

Then, by proceeding analogously to as disclosed in Example 1, 82.4 g of product:



is obtained as a crystalline powder of white colour with m.p.  $>300^{\circ}\text{C}$ , with  $n = 16$  and  $m/n = 1$ , and with a phosphorus content of 9.41% (theoretical value: 9.28%).

#### Example 5

To a 1-litre reactor equipped as in Example 1, 328 g of phosphorous acid and 82 g of acetonitrile are added. The reaction mixture is gradually heated up to  $160^{\circ}\text{C}$  in 6 hours.

A crystalline product of white colour is formed.

The reaction mixture is subsequently cooled down to  $80^{\circ}\text{C}$ , 500  $\text{cm}^3$  of water is then added to the reaction mixture with good stirring, then the reaction mixture is allowed to cool down to room temperature.

The resulting product is filtered off and the filter cake is washed on the filter with a little of water.

By drying the filter cake 290 g of 1-aminoethane-1,1-diphosphonic acid is obtained as a crystalline powder of white colour with m.p. =  $265-270^{\circ}\text{C}$  (with decomposition), and with a phosphorus content of

29.4% (theoretical value: 30.24%).

600 cm<sup>3</sup> of water and 71.2 g of intermediate (XXI) are charged to the same 1-litre reactor.

The reaction mass is heated up to 80°C and 41.0 g of 1-aminoethane-1,1-diphosphonic acid is added with stirring.

5 The reaction mixture is heated up to boiling, and is kept approximately 8 hours under refluxing conditions.

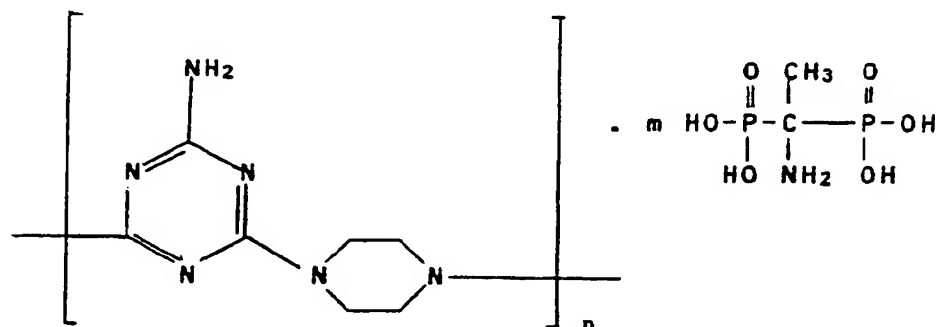
The reaction mixture is then cooled down to room temperature, the resulting product is filtered off and the filter cake is washed on the filter, with water.

After drying the filter cake, 112.2 g of product:

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is obtained as a crystalline powder of white colour with m.p. >300°C, with  $n = 15$  and  $m/n = 0.5$ , and with a phosphorus content of 10.87% (theoretical value: 11.05%).

#### Example 6

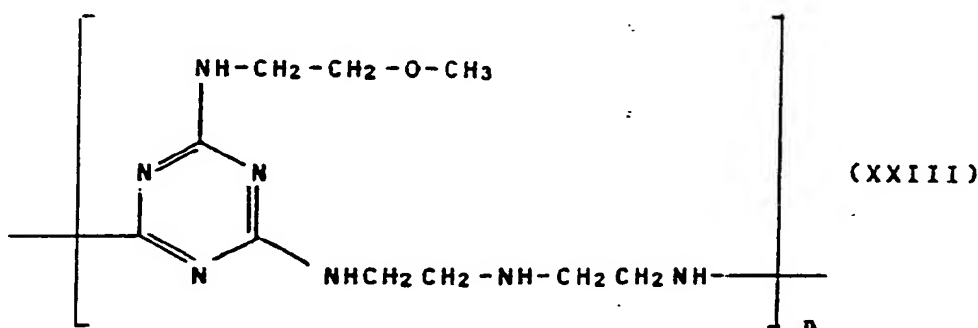
30 To a 1-litre reactor equipped as in Example 1, 350 cm<sup>3</sup> of xylene, 30 cm<sup>3</sup> of water, 66.9 g of intermediate (XVI), and, with stirring and during about 15 minutes, 30.9 g of diethylenetriamine are added.

Then, by subsequently proceeding according to the same operating modalities as disclosed in Example 1 (in this case, 24 g of sodium hydroxide is used), 72.8 g of intermediate (XXIII):

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is obtained as a crystalline powder of white colour with m.p. >300°C, and with  $n = 18$ .

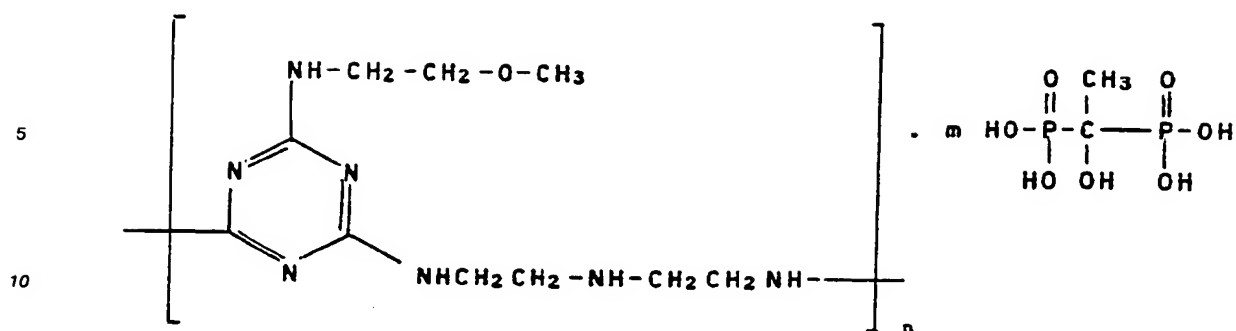
600 cm<sup>3</sup> of water, 75.9 g of intermediate (XXIII) and, with stirring and during 15 minutes, 61.8 g of a solution at 60% by weight of 1-hydroxyethane-1,1-diphosphonic acid are added to the same 1-litre reactor.

50 The reaction mass is heated up to boiling temperature, and is kept refluxing for 12 hours.

The reaction mass is cooled down to room temperature, the resulting product is filtered off and the filter cake is washed on the filter, with water.

By oven-drying the filter panel at 100°C, 111.8 g of product:

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is obtained as a crystalline powder of white colour with m.p.  $>300^{\circ}\text{C}$ , with  $n = 18$  and  $m/n = 0.6$ , and with a phosphorus content of 9.64% (theoretical value: 9.88%).

#### Examples 7-15

By operating under analogous conditions to as disclosed in Examples 1-6, the products with general formula (I) are prepared, which are reported in following Table 2.



Table 2


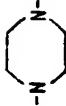



Example N.	R---N---R <sub>1</sub>	- Z -	n	m/n	$\begin{array}{c} \text{O} \\   \\ \text{HO}-\text{P}-\text{R}_3 \\   \\ \text{R}_2 \end{array}$	Melting point (°C)	Phosphorus content, %	
							Computed	Found
7	CH <sub>2</sub> CH <sub>2</sub> OH		20	1	H <sub>3</sub> PO <sub>4</sub>	>300	9.69	9.42
8	CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> OCH <sub>3</sub>		22	1	H <sub>3</sub> PO <sub>4</sub>	218-224	8.91	8.78
9	H		15	0.5	H <sub>3</sub> PO <sub>4</sub>	>300	6.83	6.67
10	H		15	1	$\begin{array}{c} \text{O} \\   \\ \text{HO}-\text{P} \\   \quad   \\ \text{C}_6\text{H}_5 \quad \text{OH} \end{array}$	>300	9.23	9.02
11	CH <sub>3</sub>	-HN(CH <sub>2</sub> ) <sub>6</sub> NH-	21	1	H <sub>3</sub> PO <sub>4</sub>	>300	8.52	8.68
12	CH <sub>2</sub> CH <sub>2</sub> OH CH <sub>2</sub> CH <sub>2</sub> OCH <sub>3</sub>	-HNC <sub>2</sub> H <sub>4</sub> -N-C <sub>2</sub> H <sub>4</sub> NH- 	18	1	H <sub>3</sub> PO <sub>3</sub>	>300	7.56	7.41

Table 2 (continued)

Example N.	R---N---R <sub>1</sub>	- Z -	n	m/n	$\begin{array}{c} \text{O} \\   \\ \text{HO}-\text{P}-\text{R}_3 \\   \\ \text{R}_2 \end{array}$	Melting point (°C)	Phosphorus content, %	
							Computed	Found
13	CH <sub>2</sub> CH <sub>2</sub> OCH <sub>3</sub>		16	1	H <sub>3</sub> PO <sub>4</sub>	>300	8.71	8.47
14	H	-HNCH <sub>2</sub> CH <sub>2</sub> NH-	17	0.4	$\begin{array}{c} \text{O} \quad \text{O} \\   \quad   \\ \text{HO}-\text{P}-\text{O}-\text{P}-\text{OH} \\   \quad   \\ \text{HO} \quad \text{OH} \end{array}$	>300	11.11	10.96
15	H		15	0.5	$\begin{array}{c} \text{O} \quad \text{O} \quad \text{O} \\   \quad   \quad   \\ \text{HO}-\text{P}-\text{C}-\text{P}-\text{OH} \\   \quad   \quad   \\ \text{HO} \quad \text{OH} \quad \text{OH} \end{array}$	>300	11.03	11.27
16	tert.-C <sub>4</sub> H <sub>9</sub>		24	1	H <sub>3</sub> PO <sub>4</sub>	>300	9.33	9.48
17			18	1	H <sub>3</sub> PO <sub>4</sub>	>300	9.39	9.21

Tables 3 and 4

The tests reported in these tables relate to polymeric compositions containing the products of general formula (I) prepared according to the preceding examples.

## EP 0 537 837 A1

Specimens consisting of approximately 3 mm thick slabs were prepared by moulding blends of granular polymers and additives, on a MOORE platen press, with a moulding time of 7 minutes under a pressure of 40 kg/cm<sup>2</sup>.

On the resulting slabs, the self-extinguishment level was determined by measuring the oxygen index (L.O.I. according to ASTM D-2863/77) on a Stanton RedCroft instrument and applying the "Vertical Burning Test", which makes it possible the material to be classified at three levels (94 V-0, 94 V-1, 94 V-2, according to UL 94 standard procedures (issued by Underwriters Laboratories - U.S.A.).

In Table 3, the values are reported which were obtained by using an isotactic polypropylene in flake form having a Melt Flow Index of 12 and a content of insolubles in boiling n-heptane of 96% by weight.

In Table 4 the values are reported which were obtained by using low-density polyethylene pellets having a Melt Flow Index of 7; polystyrene pellets containing 5% by weight of butadiene rubber and having a Melt Flow Index of 9; thermoplastic polyurethane pellets of both polyester (ESTANE 54600<sup>(R)</sup> ex Goodrich) and polyether type (ESTANE 58300<sup>(R)</sup> ex Goodrich), with specific weights of 1.19 and 1.10 g/cm<sup>3</sup> respectively ; an elastomeric ethylene-propylene copolymer with a % propylene content of 45; an acrylonitrile-butadiene-styrene terpolymer having a specific gravity of 1.06 g/cm<sup>3</sup>, a Melt Flow Index of 1.6 and containing about 40% of acrylonitrile and styrene and 20% of butadiene.

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Table 3

Example N.	Product of Example N.	Parts by weight			L.O.I. (ASTM D 2863)	UL 94 3 mm
		Product	PP(1)	AO(2)		
18	1	11.0	77	1	32.2	V0
19	2	12.0	75	1	32.0	V0
20	3	5.4	80	1	35.0	V0
21	3	19.5	70	1	33.3	V0
22	4	4.0	83	1	30.0	V2
23	4	6.3	80	1	35.5	V0
24	5	6.3	80	1	34.0	V0
25	6	5.4	80	1	34.8	V0
26	7	6.3	80	1	34.9	V0
27	8	8.0	75	1	37.4	V0
28	9	8.0	75	1	34.7	V0
29	10	12.0	75	1	31.7	V0
30	11	9.5	80	1	32.1	V1
31	12	6.3	80	1	33.0	V0
32	13	7.0	78	1	30.8	V1
33	14	6.3	80	1	32.4	V0
34	15	4.6	83	1	29.8	V2
35	15	6.3	80	1	34.8	V0
36	16	12.0	75	1	34.4	V0
37	17	12.0	75	1	36.0	V0
38	15	8.0	75	1	37.9	V0
39	4	12.0	75	1	35.8	V0
					[3] 12.0	

(1) PP = polypropylene

APP = ammonium polyphosphate -- Exolit 422(R)  
(Hoechst)

\* = APP microencapsulated with Exolit 462(R)  
melamine-formaldehyde resin (Hoechst)

(2) AO = Antioxidant

A mixture constituted by 2 parts of dilauryl-  
thio propionate and 1 part of  
pentaerythritol tetra-[3-(3,5-di-tert.-butyl-  
4-hydroxyphenyl)-propionate]

(3) = APP was replaced by monoammonium salt of 1-  
aminoethane-1,1-diphosphonic acid.

Table 4

Example N.	Polymeric support	Product of Example N.	Parts by weight			L.O.I. (ASTM D 2863)	UL 94 3 mm
			Product	Polymer	AO [2]	APP [1]	
40	LDPE	1	7.3	70	1	21.7	V0
41		3	6.4	70	1	22.5	V0
42		4	5.3	75	1	18.7	V0
43		15	14.5	70	1	14.5	V0
44	HIPS	3	8.5	65	1	25.5	V0
45		10	7.3	70	1	21.7	V0
46	PU (ester)	3	16.0	75	1	8.0	V0
47		5	16.0	75	1	8.0	V0
48	PU (ether)	5	19.4	70	1	9.7	V0
49	PP/PE	4	12.0	75	1	12.0	V0
50	ABS	10	7.0	71	1	21.0	V0

(1) APP = ammonium polyphosphate -- Exolit 422(R)  
(Hoechst)

(2) LDPE = low-density polyethylene

HIPS = polystyrene containing 5% of butadiene rubber

(ester) PU = Polyester polyurethane

(ether) PU = Polyether polyurethane

PP/PE = propylene-ethylene copolymer

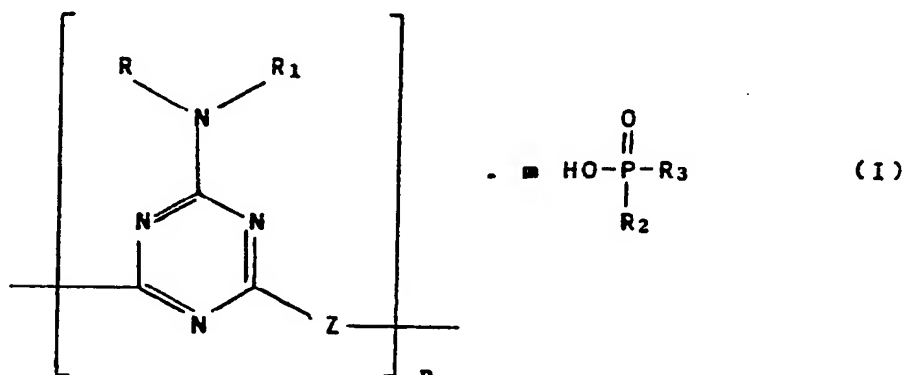
ABS = acrylonitrile-butadiene-styrene terpolymer

(3) A0 = Antioxidant

A mixture constituted by 2 parts of dilauryl-thio propionate and 1 part of pentaerythritol tetra-[3-(3,5-di-tert.-butyl-4-hydroxyphenyl)-propionate]

### Claims

1. Salts of triazinic compounds with phosphorus oxyacids, having the general formula (I):



wherein:

R is H or

$-\text{C}_p\text{H}_{2p}-\text{O}-\text{R}_4$

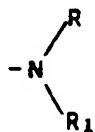
in which

p is an integer comprised within the range of from 2 to 8; and

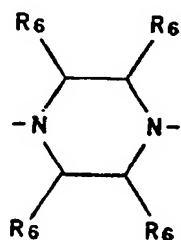
R<sub>4</sub> is H; (C<sub>1</sub>-C<sub>8</sub>)-alkyl; (C<sub>2</sub>-C<sub>8</sub>)-alkenyl;

$-\text{C}_q\text{H}_{2q}-\text{O}-\text{R}_5$ ,

in which  
 q is an integer comprised within the range of from 1 to 4; and  
 R<sub>5</sub> is H or (C<sub>1</sub>-C<sub>4</sub>)-alkyl; (C<sub>6</sub>-C<sub>12</sub>)-cycloalkyl or alkylcycloalkyl;  
 R<sub>1</sub> is (C<sub>1</sub>-C<sub>4</sub>)-alkyl or R;  
 or the moiety:

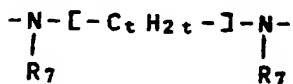


is replaced by a heterocyclic radical bonded to the triazinic ring through the nitrogen atom;  
 n is an integer comprised within the range of from 2 to 50;  
 m is a numeral smaller than, or equal to, n; in particular, the ratio of m/n is comprised within the range of from 0.5 to 1;  
 Z is a divalent or polyvalent radical falling within the scope of one of following formulae:

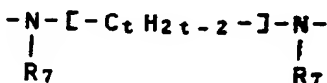


( I I )

wherein the -R<sub>6</sub> radicals, which may be the same, or different from each other, are hydrogen or (C<sub>1</sub>-C<sub>4</sub>)-alkyl;

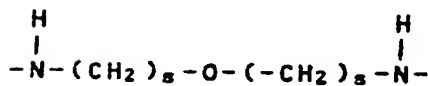


( I I I )

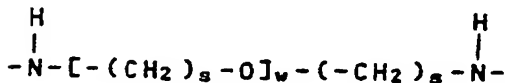


( I V )

wherein t is an integer comprised within the range of from 2 to 14; R<sub>7</sub> is hydrogen, (C<sub>1</sub>-C<sub>4</sub>)-alkyl, (C<sub>2</sub>-C<sub>6</sub>)-alkenyl, (C<sub>1</sub>-C<sub>4</sub>)-hydroxyalkyl;



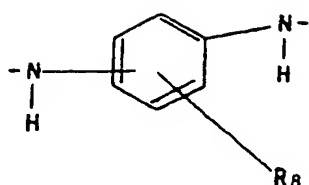
( V )



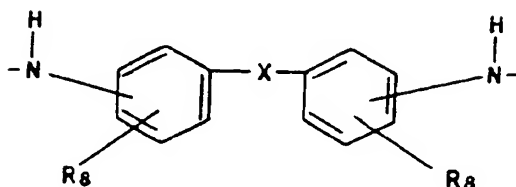
( V I )

wherein s is an integer comprised within the range of from 2 to 5 and w is an integer comprised within the range of from 1 to 3;





(VII)



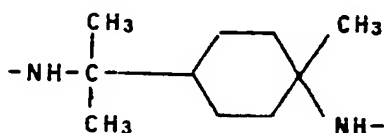
(VIII)

wherein:

X is a direct -C-C-; O; S; S-S; SO; SO<sub>2</sub>; NH; NHSO<sub>2</sub>; NHCO; N=N; CH<sub>2</sub> bond;R<sub>8</sub> is hydrogen; hydroxy; (C<sub>1</sub>-C<sub>4</sub>)-alkyl; (C<sub>1</sub>-C<sub>4</sub>)-alkoxy;

(IX)

wherein "A" can be a saturated or unsaturated cycle;

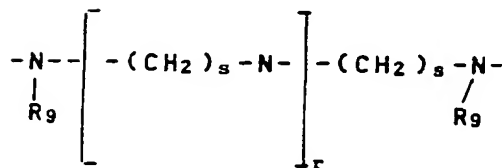


(X)



(XI)

wherein s has the above defined meaning;



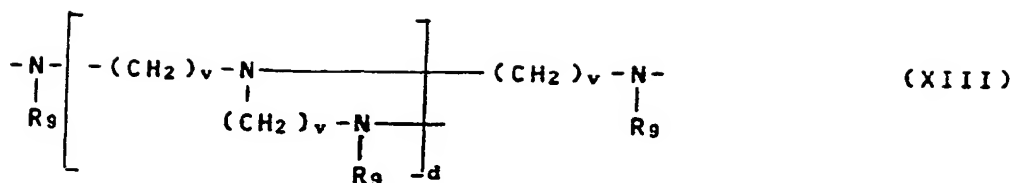
(XII)

wherein:

R<sub>9</sub> is hydrogen or (C<sub>1</sub>-C<sub>4</sub>)-alkyl;

r is an integer comprised within the range of from 1 to 5;

the indexes s, which are the same, or may be different from each other, have the above defined meaning;



wherein:

$\text{R}_9$  has the above defined meaning;

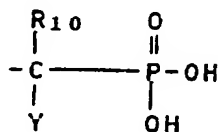
$v$  is an integer comprised within the range of from 2 to 4;

$d$  is either 1 or 2;

$\text{R}_2$  is H; OH;  $-\text{O}-(\text{C}_1-\text{C}_8)\text{-alkyl}$ ;  $-\text{O}-(\text{C}_6-\text{C}_{12})\text{-aryl}$ , possibly substituted with a  $(\text{C}_1-\text{C}_8)\text{-alkyl}$ ;  $(\text{C}_7-\text{C}_{16})\text{-aralkyl}$ ;  $(\text{C}_1-\text{C}_4)\text{-alkyl}$  possibly substituted with a carboxy group;  $(\text{C}_6-\text{C}_{12})\text{-aryl}$ ;

$\text{R}_3$  is H; OH;  $-\text{O}-(\text{C}_1-\text{C}_8)\text{-alkyl}$ ;  $-\text{O}-(\text{C}_6-\text{C}_{12})\text{-aryl}$ ,  $(\text{C}_1-\text{C}_4)\text{-alkyl}$ ;  $(\text{C}_6-\text{C}_{12})\text{-aryl}$ ;

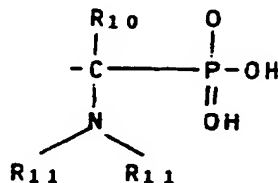
$\text{R}_3$  furthermore is:



wherein:

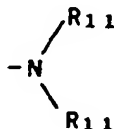
$\text{R}_{10}$  is hydrogen or  $(\text{C}_1-\text{C}_{12})\text{-alkyl}$ ;

$\text{Y}$  is OH or  $\text{R}_{10}$ ;



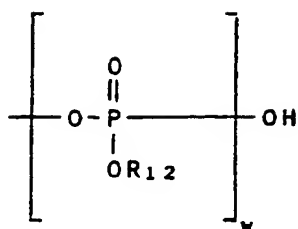
wherein:

$\text{R}_{10}$  has the same meaning as defined hereinabove and  $\text{R}_{11}$  radicals, which are the same, or may be different from each other, are hydrogen or  $(\text{C}_1-\text{C}_4)\text{-alkyl}$ ; or the moiety:



is replaced by a heterocyclic radical bonded to the carbon atom through the nitrogen atom and possibly containing another heteroatom preferably selected from O, S, N;

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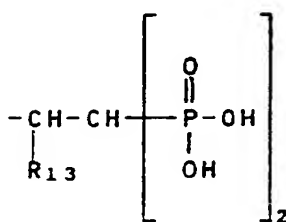


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wherein:  
 $R_{12}$  is hydrogen or  $(C_1-C_8)$ -alkyl; and  
 $w$  has the same meaning as defined hereinabove;

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wherein:  
 $R_{13}$  is hydrogen or hydroxy;

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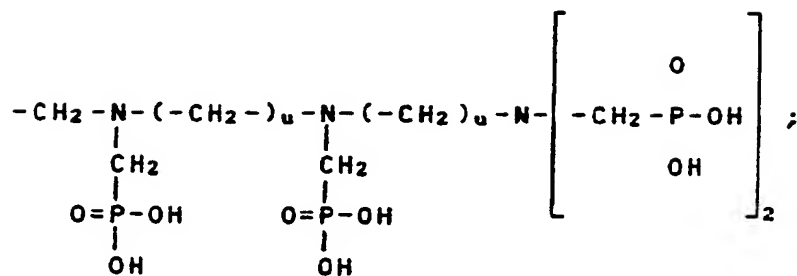
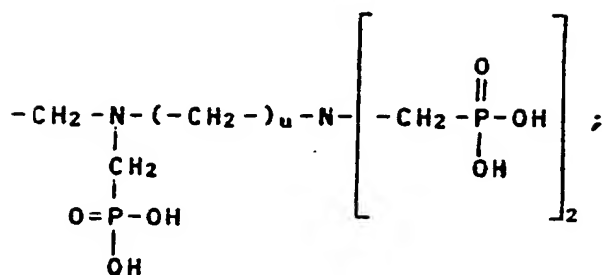
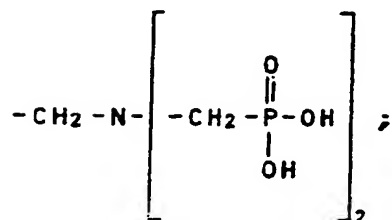
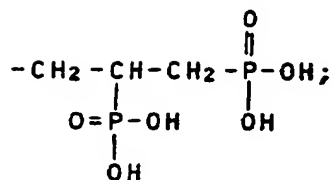
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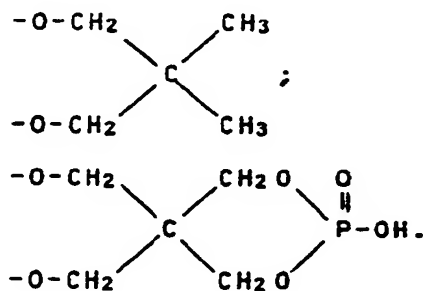
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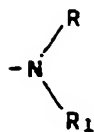
wherein:

u has the same meaning as defined above;  
or

R<sub>2</sub> and R<sub>3</sub>, taken together, may constitute a cyclic structure having the formula:



2. Salts of triazinic compounds with phosphorus oxyacids according to claim 1, wherein the moiety:



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is replaced by a heterocyclic radical selected from: aziridine; pyrrolidine; piperidine; piperazine.

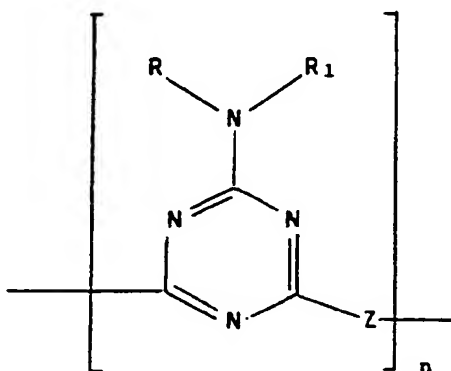
3. Salts of triazinic compounds with phosphorus oxyacids according to claims 1 or 2, in which said phosphorus acid is selected from:
- hypophosphorous acid; phosphorous acid; phosphoric acid; pyrophosphoric acid; tripolyphosphoric acid; ethane-1,1,2-triphosphonic acid; 2-hydroxyethane-1,1,2-triphosphonic acid; propane-1,2,3-triphosphonic acid; isopropylphosphoric acid; n-butylphosphoric acid; di-n-butylphosphoric acid; di-isopropylphosphoric acid; di-n-pentylphosphoric acid; isooctylphosphoric acid; hexylphosphoric acid; 2-ethylhexylphosphoric acid; methylphosphonic acid; ethylphosphonic acid; n-propylphosphonic acid; n-butylphosphonic acid; aminomethylphosphonic acid; phenylphosphoric acid; phenylphosphonic acid; phenylphosphinic acid; di-n-butylpyrophosphoric acid; di-(2-ethylhexyl)pyrophosphoric acid; octylphenylphosphoric acid; 2-methylbenzylphosphonic acid; 1-aminoethane-1,1-diphosphonic acid; 1-hydroxyethane-1,1-diphosphonic acid; 1-hydroxydodecane-1,1-diphosphonic acid; 1-(N-methylamino)-ethane-1,1-diphosphonic acid; N,N-dimethylaminoethane-1,1-diphosphonic acid; N-butylaminomethane-1,1-diphosphonic acid; phosphonoacetic acid; 2-phosphonopropionic acid; 3-phosphonopropionic acid; 2-phosphonobutyric acid; 4-phosphonobutyric acid; 2-hydroxy-5,5-dimethyl-2-oxo-1,3,2-dioxophosphorinane; 3,9-dihydroxy-2,4,8,10-tetraoxo-3,9-diphosphaspiro-[5,5]-undecane-3,9-dioxido; amino-tris(methylenephosphonic) acid; ethylenediaminetetra(methylene-phosphonic) acid; hexamethylenediaminetetra(methylene-phosphonic) acid; diethylenetriaminopenta(methylenephosphonic) acid; and so forth.

4. Process for preparing the salts having the general formula (I), comprising reacting an oligomeric derivative of 2,4,6-triamino-1,3,5-triazine, having the general formula (XIV):

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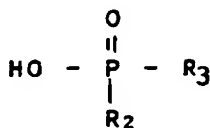


(XIV)

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wherein R, R<sub>1</sub>, Z and n have the same meaning as defined in above claim 1, with a phosphorus-containing acid having the general formula (XV):

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(XV)

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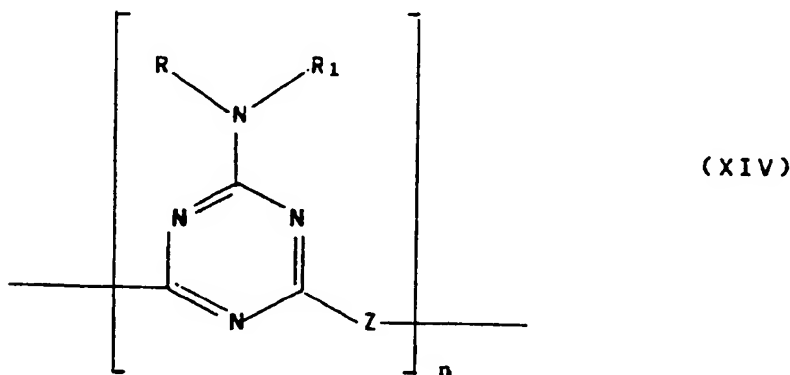
wherein R<sub>2</sub> and R<sub>3</sub> have the same meaning as defined in above claim 1.

5. Process according to claim 4, wherein the reaction between the derivatives having the general formula (XIV) and the phosphorus-containing acids having the general formula (XV) is carried out in the

presence of a solvent, at temperatures comprised within the range of from 0° C to the boiling point of the solvent.

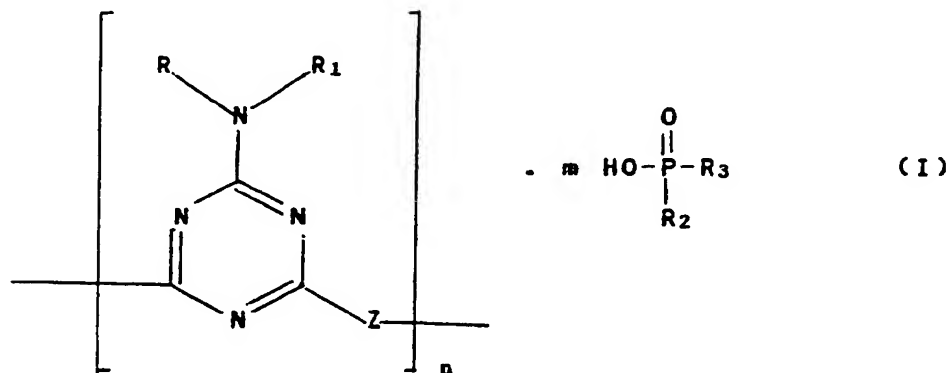
6. Self-extinguishing polymeric compositions comprising:

- (a) from 90 to 40 parts by weight of a thermoplastic polymer, or of a polymer with elastomeric properties;  
 (b) from 7 to 28 parts by weight of one or more ammonium or amine phosphate(s) or phosphonate(s);  
 (c) from 3 to 32 parts by weight of one or more oligomeric derivative(s) of 2,4,6-triamino-1,3,5-triazine salified with a phosphorus oxyacid, said oligomeric derivatives of 2,4,6-triamino-1,3,5-triazine having the general formula (XIV):



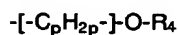
wherein R, R<sub>1</sub>, Z and n have the same meaning as defined in claim 1.

7. Self-extinguishing polymeric compositions according to claim 6, in which the (c) component preferably is selected from the salts having the general formula (I):



wherein R, R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub> radicals, Z, n and m have the meaning defined in claim 1.

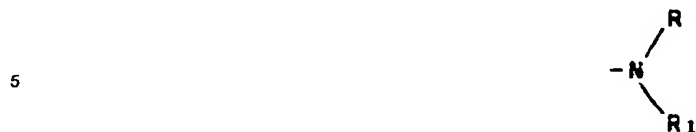
8. Self-extinguishing polymeric compositions according to claims 6 or 7, in which the R radical is replaced by a



moiety, in which p is an integer comprised within the range of from 2 to 4 and R<sub>4</sub> is hydrogen or (C<sub>1</sub>-C<sub>4</sub>)-alkyl.

9. Self-extinguishing polymeric compositions according to claims 6, 7 or 8, in which R<sub>1</sub> radical is hydrogen.

10. Self-extinguishing polymeric compositions according to claims 6 or 7, in which the moiety:



in general formula (XIV) is replaced by an  $-\text{NH}_2$  radical.

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11. Self-extinguishing polymeric compositions according to claims 7 or 8, in which the moiety:

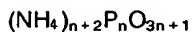


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in general formula (XIV) is replaced by a heterocyclic radical selected from among aziridine, pyrrolidine, piperidine, piperazine.

12. Self-extinguishing polymeric compositions according to any of claims from 6 to 11, in which ammonium phosphate(s) (b) has(have) the general formula

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wherein n is an integer equal to or larger than 2.

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13. Self-extinguishing polymeric compositions according to any of claims from 6 to 11, in which ammonium phosphate(s) (b) has(have) the general formula



wherein n is a numeral comprised within the range of from 50 to 500.

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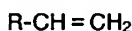
14. Self-extinguishing polymeric compositions according to any of claims from 6 to 11, in which amine phosphate(s) (b) is(are) selected from dimethylammonium or diethylammonium phosphate; ethylenediamine phosphate; melamine ortho- or pyrophosphate.

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15. Self-extinguishing polymeric compositions according to any of claims from 6 to 11, in which ammonium phosphonate(s) (b) is(are) mono- and polyphosphonates.

16. Self-extinguishing polymeric compositions according to any of claims from 6 to 15, in which the polymer (a) is selected from the polymers and copolymers of olefines having the general formula

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in which R is a hydrogen atom, or a  $\text{C}_1$ - $\text{C}_8$  alkyl or aryl radical; acrylonitrile/butadiene/styrene (ABS) terpolymers; styrene/acrylonitrile (SAN) copolymers; polyurethane; poly(ethylene terephthalate); poly(butylene terephthalate); polyamides.

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17. Self-extinguishing polymeric compositions according to claim 16, in which olefin polymers and copolymers are selected from

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1. isotactic or prevailing isotactic polypropylene;
2. HDPE, LLDPE, LDPE polyethylene;
3. crystalline propylene copolymers containing minor proportions of ethylene and/or other  $\alpha$ -olefins, such as 1-butene, 1-hexene, 1-octene, 4-methyl-1-pentene;
4. heterophasic compositions comprising

(A) a fraction consisting of a propylene homopolymer, or of one of the copolymers according to (3); and

(B) a copolymeric fraction formed by elastomeric copolymers of ethylene with an alpha-olefin, possibly containing minor proportions of a diene, in which the alpha-olefin is preferably selected from propylene and 1-butene;

5. elastomeric copolymers of ethylene with alpha-olefins possibly containing minor proportions of a diene.

18. Moulded articles of manufacture, obtained from the compositions according to the preceding claims.





European Patent  
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## EUROPEAN SEARCH REPORT

Application Number

EP 92 20 3074

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
Y	EP-A-0 448 774 (MINISTERO DELL'UNIVERSITA' E DELLA RICERCA SCIENTIFICA E TECNOLOGICA) * the whole document * ---	1,6-18	C07D251/70 C08K5/3492 C08K5/49 C07F9/38
Y	EP-A-0 415 371 (MINISTERO DELL'UNIVERSITA' E DELLA RICERCA SCIENTIFICA E TECNOLOGICA) * the whole document * ---	1,6-18	C07F9/48 C07F9/6574 C07F9/11
Y	EP-A-0 286 478 (ATOCHM) * the whole document * ---	1,6-18	
P,Y	EP-A-0 453 871 (MINISTERO DELL'UNIVERSITA' E DELLA RICERCA SCIENTIFICA E TECNOLOGICA) * the whole document * ---	1,6-18	
P,Y	EP-A-0 466 137 (MINISTERO DELL'UNIVERSITA' E DELLA RICERCA SCIENTIFICA E TECNOLOGICA) * the whole document * -----	1,6-18	
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			C07D C07F C08K
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 17 DECEMBER 1992	Examiner BESLIER L.M.
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		I : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons ----- & : member of the same patent family, corresponding document	

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